Physics of Functional Materials and Devices

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Lecture – 25, Week 6

Thermogravimetric (TGA) analysis

Welcome to the final lecture of week 6. Till now we have been talking to you about the thermal properties in solids. We started from expansion, then we went on to talk to you about the heat capacities, the latent heats and how these properties can change near a phase transition or you can also change these properties in materials just by changing the composition or the density of these materials. A very important question which is always asked by students is how do we measure these changes or we believe that there are some modifications taking place. in the thermal properties in solids, how do we actually measure? So, let us spend a lecture to understand the common techniques by which you can find out the variation in materials as a function of changing thermal energy. And so, we will talk to you about the thermal analysis techniques which are used in today's research and industries to characterize the thermal properties of solids.

Why should mass change as a function of changing temperature and if mass changes then you have a common technique which is called as thermogravimetric analysis that is TGA and how do you analyze these thermograms to understand the thermal properties of solids. There are various types of thermal analysis and a material is characterized by all these techniques before you get a broad idea about the thermal properties of solids. For example, if you are analyzing the change in the weight of the sample as a function of changing temperature, then the technique is called as thermogravimetric analysis. But if you do not find the change in mass, but your interest is to determine the change in heat near the transitions.

It could be phase transitions or it could be just a transition from one point to the other what kind of analysis you undertake that is called the differential thermal analysis that is DTA. You have already seen how do we determine the thermal expansion in solids you measure using dielectrometry, but if you have other technique then this technique iscalled as thermal mechanical analysis TMA. When a phase transition takes place what are you doing? Either you get heat out that is endothermic or you need to supply heat near the phase transition.

So, this kind of occurrence of exothermic or endothermic reactions near the phase transformations are analyzed using differential scanning chlorimetry and if you are talking about the temperature at which gas is desorbed from a surface of the material for example, a catalyst surface. then you are talking about temperature program desorption technique TPT.

So, how will you define the thermal analysis? It is a technique to study the behavior and properties of materials as a function of changing temperature. What are the parameters that are involved it depends on what you are interested in. Once again if you are interested in mass change determination as a function of temperature you are talking about TGA, heat of transitions and the relative change DTA. Expansion variation as a function of temperature TMA, heat flow during transitions DSC and the temperature at which gas gets dissolved from a material surface you are talking about TPT. Let us start with a very common technique that is thermal gravimetric analysis TGT.

Here what are you doing? You are going to record mass change as a function of temperature variation. Obviously, you will have a material. So, you will have a sample you need to have a heater. in which the sample will be placed and then you should have a measuring system which will measure the change in mass. So, you will have micro balance-based systems which will then help you to measure the mass change.

The resulting measurement signal will give you what either you will talk in term of absolute change or relative mass change. Simple. Why should a material actually show mass loss? you can see variation in mass because of decomposition the material just gets decomposed and you have the chemical bonds getting broken and you have the release of energy or you have the volatile components just getting out of the material or you can have evaporation the volatile components are just moving out of the material you can have reduction where interaction of sample to a reducing atmosphere takes place and you have mass changes or you can have desorptions where you can just have certain material leaving from the surface or adsorbed gases on the surface are leaving the material surface. So, that will also lead to the loss in mass as a function of increasing temperature. You can have gain by processes such as oxidation or absorption or adsorption or you can have any kind of new formation or like nitride formation in materials and that would lead to increase in the weight.

These things can then be easily measured using the TGA instrument. This instrument is schematically shown in the figure in this slide. So, you have basically a heater, a sample pan which can then be introduced within a heater, you have a thermocouple to measure the temperature change and then you have the balance system and finally, you have the change of light which is then converted into current and then from there you can find out the change in mass. You can perform the same measurement under various environments. That means, you can perform TGA analysis in presence of nitrogen or in presence of argon and if you

have such kind of facilities then you will have instruments that will have the gas inlet valves and from where you can then give in the required gases.

This balance which you have the null point balance basically operates on the principle of null balance. What happens? At the 0 or null, the position equals amount of light shining on the two photodiodes. So, you have light shining on two photodiodes are same. Now, suppose you have a standard and you have the sample for which you are measuring. If you have these variations taking place, so you are measuring the mass of the second with respect to a standard plot, then if the mass moves out of the null position, what will happen? an unequal amount of light would shine on the photodiodes, but you want to have same intensity coming out of the photodiodes.

So, what will you need to do? You will have to supply current. So, you will apply a current to the meter so that the photodiodes get the equal light and the balance returns to the null position. What will that mean? That would mean the amount of current applied is proportional to the weight loss or weight gain. This is a typical weight percent versus temperature curve. So, what you see if you plot initially, you have 100 percent weight you have taken the original sample.

Now, you are heating the sample as a function of temperature you see the blue solid blue line you have the weight loss which takes place that is given by Δm. Now, you can find there are various regions in this curve and you will see that the phenomena's are slightly different in different regions. You will find that there is a region where actually initial weight loss becomes quite evident. So, you see significant change in the weight loss. and then you have the final temperature up to which you are either measuring or beyond which you see that the weight loss has started to go to a constant value.

Then you have the onset, the temperature point on the thermogram where the thermal decomposition or reaction of the sample begins. So, you have the onset temperature. Then you have an end point. The temperature point on the thermogram where the thermal decomposition or reaction of the sample is complete. If you analyze different kind of samples you may end up getting different forms of TGA curves.

If you have a curve shown in A then this means that there is insignificant weight change and the material is quite stable and you do not have adsorbed molecules on the surface of the material even water adsorption is quite low. So, you will not see significant change in these kinds of materials. Then if you see the curve B then you see certain loss in temperature initially let us say up to 100° or 150° and then the material shows insignificant change in its mass. This basically means that it is occurring because of the drying of the solvents and you have removed the solvents and the material has then become free of solvents and has attained a stable state. Then, you have a single step decomposition where you see a sudden change in the way of the material is behaving up to a certain point there

was slow rate of change of mass, but beyond that temperature there is a sudden loss in the mass and if there is a sudden loss that means the material has got decomposed.

You can have multi step decomposition you will see you can have multi point decompositions or you can see weight gain where the material is going through the process of oxidation. So, what would be the factors that would affect the TGA curves? There would be heating rates. If you heat the material very fast, then it is unable to obtain equilibrium states and you do not have the right nature coming out because the material is unable to respond instantaneously to the change in heat around it. If you have a very small sample or if you have a very large sample then that would affect the TGA curves. if you have very dense system or you have a very porous system or you have a particle size which is forming this material to be very large or you have a smaller size particle of the material then that would affect the nature of the TGA curves.

The sample holder that is the crucible shape and type can also affect the TGA curve. So, you must run an empty crucible TGA curve and then you must subtract that behavior from the obtained curve. So, that you do not get artifacts which may come in from the TGA behavior of the crucible or the sampler itself. The rate at which the gas flow occurs if you are performing these measurements under different conditions can also affect and obviously, if you have oxygen, if you have nitrogen, if you have argon, if you change the nature of the gas which is being put inside the chamber when the measurement is taking place that can also affect the nature of the TGA curves. If you see all the curves which we have shown, using these curves the TGA data can be utilized to obtain information about activation energy, thermal stability, drying temperatures, burning points and ash contents, materials identification and purity assessment, composition of materials corrosion and chemical behavior of the materials, thermal aging effects, you can talk in terms of glass transition temperatures, the melting temperatures, the reinforcement temperatures.

So, you can have wide range of applications for the TGA analysis. So, again questions? will all the materials having the same density show similar TGA curves. So, I give you materials which have same density. Will they have similar TGA behavior? Yes, or no? Obviously, they would have different behavior. Why? Because you will have different elements forming that material and they will have different heat capacities latent heats.

And that means, you will have different phase transitions taking place and you will have different orders of activation energy or various types of activation barriers which would be different in these materials even if they have the same densities. This is one of the answers. Can you list the reason why different materials will have different TGA curves? So, now you have understood that there are techniques which can be used to characterize the thermal properties of solids. Before the material is used in any applications, these properties must be thoroughly characterized. In this lecture, we just talked to you about the TG analysis,

but other analysis such as TMA, DTA and other thermal analysis must be performed before a material goes into a device.

You must now be understanding that why it takes time for a material to go into final application after it has been successfully synthesized. Because, after the synthesis of the material there are a series of steps which must be followed before the device can be fabricated and that step or those steps are called as characterization of materials and in this week, we talked to you about the thermal characterization of solids. And in the next week we will talk to you about the next round of characterizations which must be perform before we start talking about the use of the synthesized material in devices. These are the books which you can follow to develop further understanding and I thank you once again for attending this 12-week course on physics of functional materials and devices.